NACA RM E53I17

NACA

RESEARCH MEMORANDUM

SPONTANEOUS FLAMMABILITY OF PENTABORANE AND PENTABORANE - 3-METHYLPENTANE BLENDS

By Edward A. Fletcher

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

WASHINGTON

February 13, 1957
Declassified September 17, 1958

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

SPONTANEOUS FLAMMABILITY OF PENTABORANE AND PENTABORANE - 3-METHYLPENTANE BLENDS

By Edward A. Fletcher

3119

SUMMARY

A study has been made of the spontaneous flammability of pentaborane and pentaborane - 3-methylpentane blends. The behavior of these substances in air in both the liquid and vapor states was studied.

Stoichiometric pentaborane vapor - air mixtures are not spontaneously flammable at temperatures up to 100° C, but the presence of liquid pentaborane will result in ignition at much lower temperatures. Liquid pentaborane can react with air and probably thus raise itself to the kindling temperature.

Dilution of liquid pentaborane with 3-methylpentane reduces the tendency to ignite spontaneously.

INTRODUCTION

Interest in the use of pentaborane and pentaborane-hydrocarbon blends as aircraft fuel has resulted in a need for information about the flammability of these fuels and the behavior which both the liquids and vapors might be expected to exhibit on contact with air during various operations involving their use. Some observations are reported herein that were made in the course of handling pentaborane at the NACA Lewis laboratory, as these observations are related to the hazards involved, and a number of experiments are described that were made to determine those conditions under which pentaborane might be expected to ignite spontaneously and those under which it might be safely handled in experimental work.

Available information on the subject is somewhat contradictory. Reference 1 states that pentaborane is not spontaneously flammable. The authors of reference 2 observed initially that pentaborane was not spontaneously flammable in air. They describe an accident in which a glass vial containing 2 grams of the liquid was broken and its contents spilled onto a laboratory bench; although the pentaborane evaporated rapidly, there was no flame. Nor did flame result when air was admitted into an evacuated vessel containing frozen pentaborane which was then

3119

allowed to evaporate slowly. Under other conditions, however, when pentaborane was allowed to evaporate rapidly into air, or when air was rapidly admitted into a bulb containing pentaborane vapor, or when a mixture of pentaborane with air was allowed to expand into a warm evacuated bulb, flames resulted. That this behavior might be due to the presence of impurities was investigated and found to be unlikely.

Reference 3 reports that pentaborane-air mixtures could not be prepared over a very wide range of compositions, inasmuch as they were spontaneously flammable.

In view of these apparent contradictions, a qualitative investigation was made of the behavior of both pentaborane liquid and vapor in air at various temperatures, and of pentaborane blends with 3-methylpentane. 3-Methylpentane was chosen because its vapor pressure over a wide range of temperatures is close to that of pentaborane. Included are the preparation and heating of stoichiometric mixtures of pentaborane with air at atmospheric pressure, spraying of pentaborane into air, the impingement of pentaborane and pentaborane - 3-methylpentane mixtures against a heated surface, and the determination of the spontaneous ignition temperatures of pentaborane and various pentaborane - 3-methylpentane mixtures. The possibility of spontaneous inflammation resulting from 10 cubic centimeter spills of the liquid was also investigated.

PROCEDURE AND RESULTS

Conditions Under Which Pentaborane Did Not Ignite

Preparation of stoichiometric mixtures. - No ignition resulted when small amounts of pentaborane were admitted to air at room temperature or below. Thus, it was possible to prepare stoichiometric pentaborane-air mixtures in two ways:

1. The first method is essentially that of Schlesinger (ref. 2). A 200 cubic centimeter round-bottom flask was sealed off at the neck and equipped with a stopcock and joint for attachment to a conventional vacuum line. This served as the vessel for preparation and study of the fuel-air mixtures. Pentaborane was admitted to the flask to a pressure of 27 millimeters and then frozen out in the bottom by immersion in a liquid nitrogen bath. The nitrogen bath was then raised until the entire flask was immersed and air was admitted to a pressure of 182 millimeters. The stopcock was then closed, and the bulb placed into a 4-liter beaker which was to serve as a water bath and allowed to warm to room temperature. The total pressure in the bulb at room temperature was approximately 740 millimeters (atmospheric).

2. The second method of preparation made use of the apparatus shown in figure 1. Pentaborane was injected into the 241 cubic centimeter bulb by pulling the thin breaking wire to break off the end of the capsule. The capsules were pressurized by sealing them off while the pentaborane was frozen and the capsule filled to 1 atmosphere with nitrogen. On subsequent warming to room temperature the total pressure was greater than 1 atmosphere by the vapor pressure of pentaborane. After the capsule had been broken, the breaking wire could be removed and the stopcock closed. The condensible contents of the bulb could be recovered by attaching the bulb to a vacuum line through the standard taper joint and pumping it out through liquid nitrogen cooled traps.

Observations made during the course of preparing stoichiometric pentaborane-air mixtures. -

1. No ignition resulted when sufficient pentaborane to form a stoichiometric mixture was quickly sprayed into air in a 241 cubic centimeter bulb.

2. No ignition resulted when sufficient pentaborane to form a stoichiometric mixture was allowed to evaporate into a closed bulb containing air except under a special condition. Ignition did occur when warm water was sprayed againt the bulb in an effort to speed up evaporation. In other experiments, ignition did not occur, but there was a slight amount of oxide formation in the region of the bulb where the liquid pentaborane had been. The amount of oxide was greater when warming was slower, that is, when the residence time of the liquid was longer.

3. When the pentaborane was diluted to 50 percent with 3-methylpentane, there was no evidence of any reaction even though the mixture was heated to 85° C over a $2\frac{1}{2}$-hour period and then allowed to stand at room temperature for 2 days.

4. Stoichiometric mixtures could be heated as high as 100° C (the highest temperature used) for periods of about $2\frac{1}{2}$ hours without visible evidence for reaction. However, brushing the bulbs with a bunsen burner or sparking the mixture resulted in violent explosions which either blew out the stopper or completely shattered the bulb.

5. 97 Percent of the pentaborane was recovered unchanged and identified by its vapor pressure from a stoichiometric mixture which had been prepared by the second method and allowed to stand at room temperature for 15 minutes.

Conditions Under Which Pentaborane Ignited

1. Ignition occurred when air was rapidly admitted to a 250 cubic centimeter bulb containing pentaborane vapor at 29 millimeters. The inside of the bulb was completely covered with a brown-white ash.

2. Ignition occurred when an unpressurized injection capsule containing liquid pentaborane at room temperature was suddenly broken to allow air to rush in on top of the liquid.

3. Impingement of liquid sprays of pentaborane and blends of pentaborane with 3-methylpentane against heated surfaces frequently resulted in ignition. The fuels were ejected from capsules similar to those shown in figure 1 by shearing off the tips with a 15-centimeter length of 8-millimeter pyrex tubing through which warm water or steam was being circulated. The 8-millimeter tubing thus served both as a tube breaker and a heated surface for impingement of the liquid fuel. The fuel components were measured and mixed in the vapor phase and the capsules were pressurized as before with nitrogen. The amount of fuel varied from about 0.03 to 0.05 cubic centimeter per capsule. The results of 24 runs in which the fuel composition was varied from 100 percent to 70 percent pentaborane and the water temperature varied from 25° to 100° C are given in figure 2. These points indicate that there is a rather sharp distinction between the temperature-composition regions which result in spontaneous ignition and those which do not. It is also noteworthy that while 100 percent pentaborane ignited at about 47° C, addition of about 20 percent 3-methylpentane raised the spontaneous-ignition temperature to above 100° C for this type of experiment.

4. In order that the relative flammability of pentaborane - 3-methylpentane blends might be compared with that of the wide variety of fuels of reference 4, spontaneous-ignition temperatures were determined in the apparatus therein described. It consisted essentially of a 125 cubic centimeter Erlenmeyer flask open to the atmosphere enclosed in an electrically heated Inconel block. Temperature was measured with an iron-constantan thermocouple inserted in the block about 1/4 inch below the flask. About 20 minutes was allowed for thermal equilibrium to be established before each of the injections and a steady temperature was ensured by the high heat capacity of the block. Approximately 0.05 cubic centimeter fuel samples were injected directly into the flask using capsules like those described above. Determinations were made with pentaborane concentrations varying between 50 and 100 percent by weight. A clean flask was used for each point. Ignition always occurred within about 2 seconds or not at all. The results of these determinations are plotted in figure 3. Of the 11 injections of pure pentaborane made between 41.5° C and 56.7° C, 5 ignited and 6 did not. The point shown for 0 percent pentaborane was taken from reference 4. The dashed curve is a superimposition of the curve taken from figure 2. A comparison of these two curves shows that the values obtained over the limited range covered by both these methods are quite similar.

5. In an effort to understand the ignition sometimes observed for large spills of pentaborane, 10 cubic centimeter samples of liquid pentaborane were squirted into an evaporating dish and into a 30 cubic centimeter test tube at 27° C. It was originally anticipated that the ignition process might be quite slow or even not take place at all, and that only relatively crude, slow instrumentation would be required to follow the reaction. The instrumentation used therefore consisted only of a pair of iron-constantan thermocouples immersed in the liquid, one just below the surface and the other as deep as was possible in the particular vessel being used; the outputs of the thermocouples were measured by millivoltmeters. The operation was very roughly timed with a photographic timer. Motion pictures at 24 frames per second were taken of the entire setup including the injection vessel, millivoltmeters, and timer. The pentaborane burst into flame in both cases. Figure 4 is taken from the motion pictures of both runs. It shows the apparatus near the beginning of the injection and the first frame in which flame appears in each run. It can be seen that there was approximately a 1-second induction period in the evaporating dish and a 2-second induction period in the test tube. The material in the evaporating dish was completely consumed. The material in the test tube stopped burning after about half of the liquid had been consumed. When the test tube was smashed and the pentaborane allowed to fall on the ground, it again burst into flame.

DISCUSSION

The observations made in this study indicate that, while gaseous pentaborane-air mixtures having low equivalence ratios are not very likely to ignite spontaneously below 100° C, liquid pentaborane can ignite in air at relatively low temperatures. Furthermore, liquid pentaborane can probably react with air and may thus raise itself to the kindling temperature quite rapidly. In this respect pentaborane is much more hazardous than other easily ignitible substances such as carbon disulfide. This was indicated in the experiments concerned with preparing stoichiometric mixtures. Oxide formation could be observed only in those regions of the flask which had been in contact with liquid; the extent of oxide formation was greater in that case where the bulb was allowed to warm up very slowly and liquid pentaborane was presumably in contact with air for a longer period of time. When the liquid pentaborane was warmed by splashing the bulb with warm water, it ignited, although similar bulbs containing only vapor and air at equivalence ratios of 1 or less could be heated as high as 100° C without ignition. When a sufficient quantity of liquid is present, it will ignite even without external heating as was demonstrated in the 10 cubic centimeter spill experiments. That pentaborane vapor at 27 millimeters was observed to ignite upon introduction of atmospheric air is not inconsistent with the conclusions reached above, since mixing is probably not immediate and there probably exist regions in such a bulb where the mixture is very rich or where the partial pressure of the fuel vapor tends to exceed the saturation pressure and condensation results.

These conclusions are also consistent with the observations of the workers cited in the introduction to this report. They observed ignitions when air was rapidly admitted to flasks containing pentaborane and when a pentaborane-air mixture was suddenly allowed to flow from one bulb into another warm evacuated bulb. The postulated reason for ignition in the first case was given in the previous paragraph. It is quite conceivable that igniton occurred in the second case because liquid droplets formed during the sudden expansion in the first bulb were carried over into the second warm bulb where they became centers of high fuel concentration.

When conditions are such that the liquid evaporates and mixes with excess air very quickly without warming up, there is no ignition. This was illustrated by the fact that ignition did not result when small amounts of pentaborane were sprayed into air or at cool surfaces.

Dilution of pentaborane with hydrocarbon raises the spontaneous ignition temperature.

Although the effects of mixture composition were not studied, gaseous pentaborane-air mixtures are probably not spontaneously flammable over a fairly wide range of concentrations, inasmuch as no ignition was observed during the vaporization of the liquid to form stoichiometric mixtures. However, in view of the fact that many operations can result in condensation to the liquid, such mixtures should be handled only with adequate safety precautions. The greater reactivity of the liquid is by no means unique in the case of pentaborane. Explosions of fuel - liquid oxygen mixtures at temperatures far below the conventional "ignition temperatures" have been observed by many workers. Such behavior has also been observed with diborane. Thus, diborane does not react with dry air or oxygen at room temperature, but the liquid kindles when suddenly brought into contact with air at temperatures as low as -120° C (ref. 5).

CONCLUSIONS

1. Stoichiometric pentaborane vapor - air mixtures are not spontaneously flammable at temperatures up to 100° C.

2. At least 97 percent of the pentaborane vapor can be recovered from a stoichiometric mixture unchanged after 15 minutes.

3. Liquid pentaborane will ignite instantly in air if sprayed against a surface warmed to about 45° C.

4. Liquid pentaborane will react with air at room temperature. If sufficient liquid is present, it will burst into flame after a short induction period.

5. Dilution of liquid pentaborane with 3-methylpentane raises the spontaneous ignition temperature to about 100° C for 80 percent pentaborane and to about 214° C for 50 percent pentaborane.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, September 17, 1953

REFERENCES

1. Stock, Alfred: Hydrides of Boron and Silicon. Cornell Univ. Press, Ithaca (New York), 1933, p. 70.

2. Schlesinger, H. I.: Boron Hydrides. NRL Rep. P-2964, Chem. Div., Navy Dept., Office Naval Res., Wash. (D.C.), July 1946. (Final Rep. on Contract 173s-10421 from Univ. Chicago.)

3. Price, F. P.: Burning and Detonation of Mixtures of Boron Hydrides with Air and Oxygen. Rep. No. 50A0504, Res. Lab., Apparatus Dept., General Electric Co. (N.Y.), Mar. 1950. (Proj. HERMES TUI-2000A, U.S. Army, Ord. Dept.)

4. Jackson, Joseph L.: Spontaneous Ignition Temperatures of Pure Hydrocarbons and Commercial Fluids. NACA RM E50J10, 1950.

5. Stock, A., Kuss, E., und Preiss, O.: Borwasserstoffe. V. Die Einwirkungvon Chlor und Brom auf B_2H_6 und $B_{10}H_{14}$. Die Wertigkeit des Bors. Ber. D. Chem. Gesell., Bd. 3, Jahrg. 47, 1914, pp. 3115-3116.

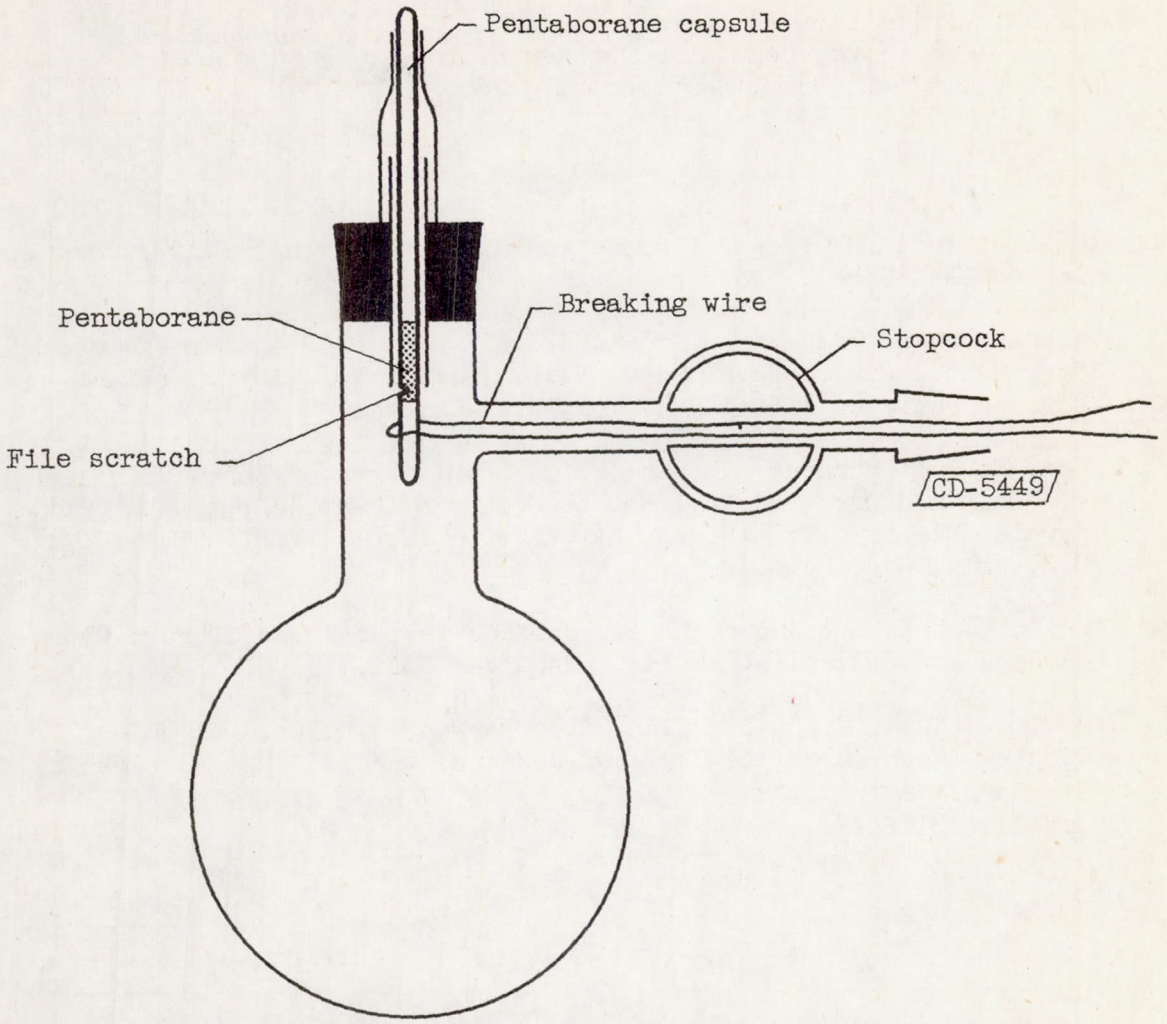


Figure 1. - Apparatus for preparation of pentaborane-air mixtures.

3119

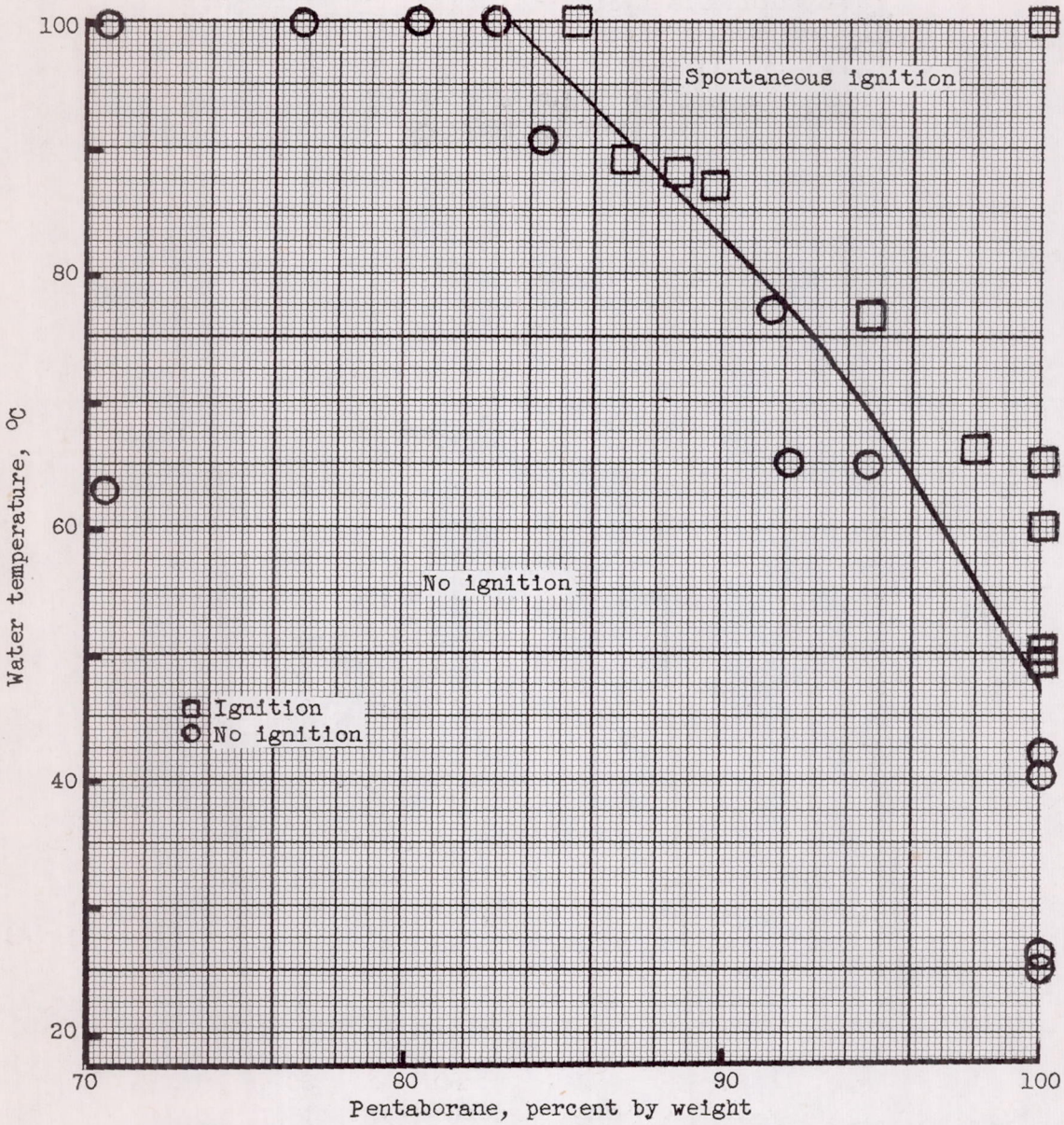


Figure 2. - Spontaneous ignition of liquid pentaborane - 3-methylpentane mixtures resulting from impingement on 8-mm tubing through which warm water was being circulated.

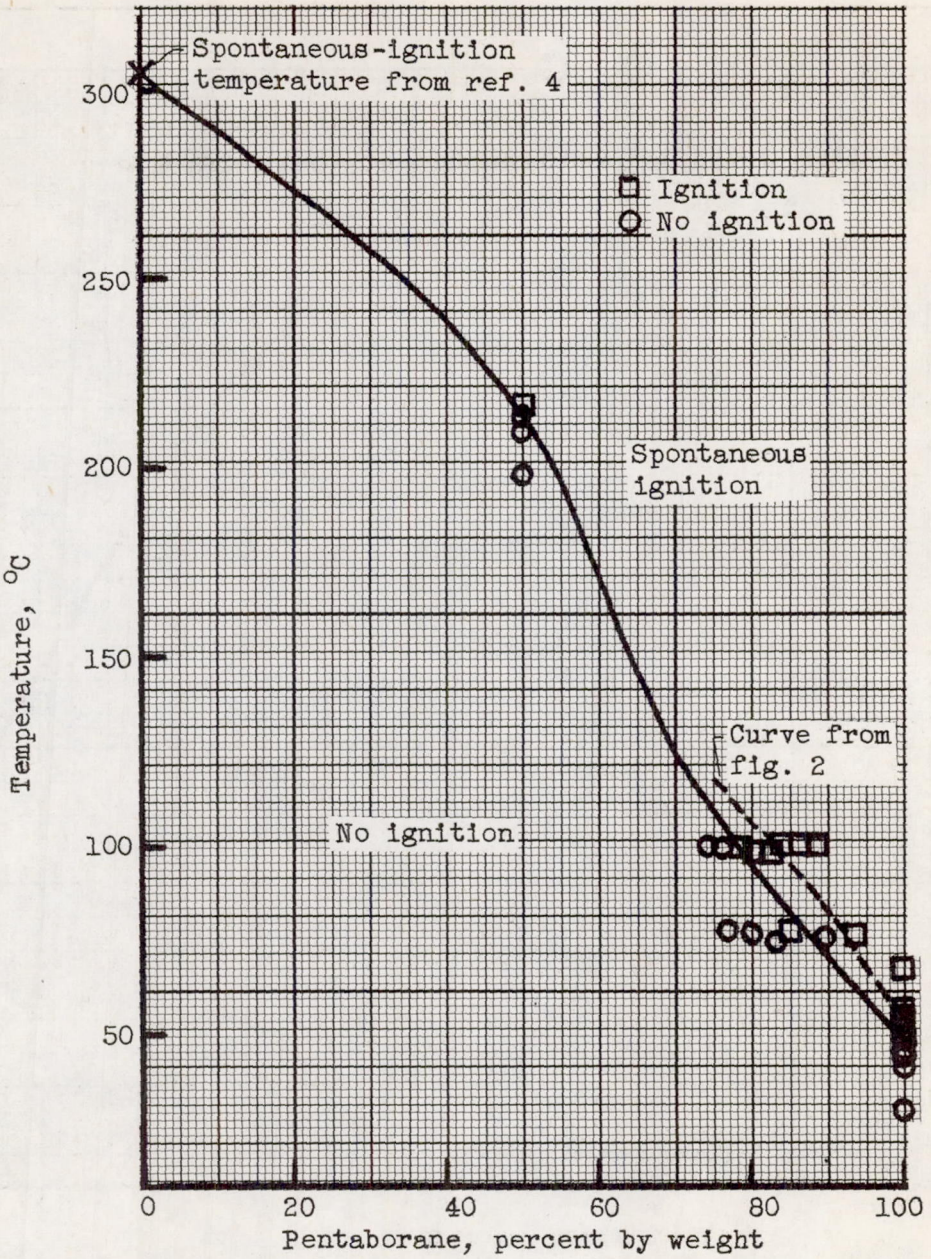
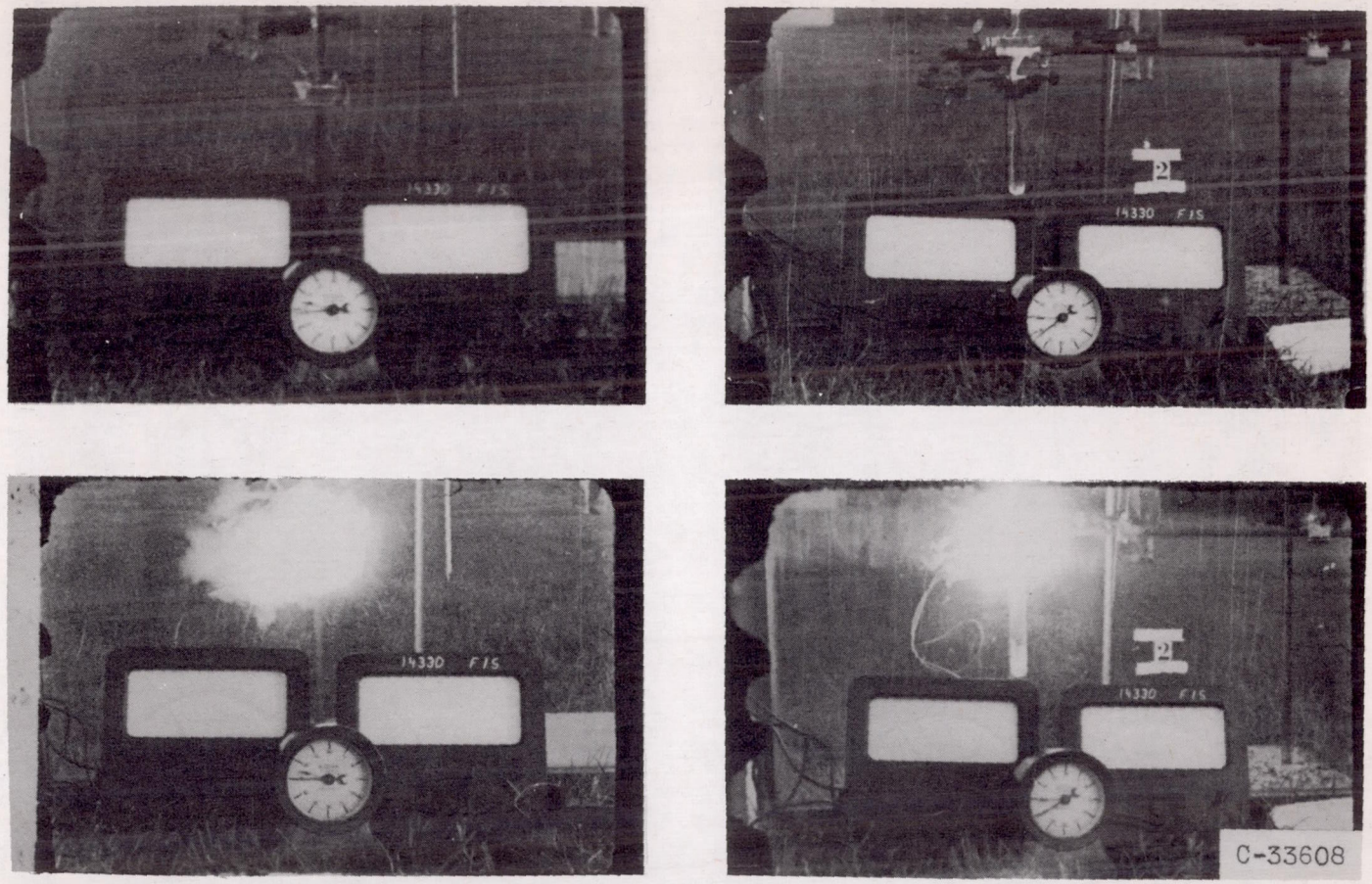


Figure 3. - Spontaneous-ignition temperatures of pentaborane - 3-methylpentane mixtures injected as a liquid.



(a) Glass evaporating dish.

(b) Test tube.

Figure 4. - Ignition of 10-cc samples of pentaborane following injection into a glass evaporating dish and a test tube. Taken from motion pictures at 24 frames per second. Upper pictures show apparatus after start of injection; lower pictures show the first frame in which flame appears.

NACA - Langley Field, Va.